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Suitability of marginal biomass-derived biochars for soil amendment

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Abstract

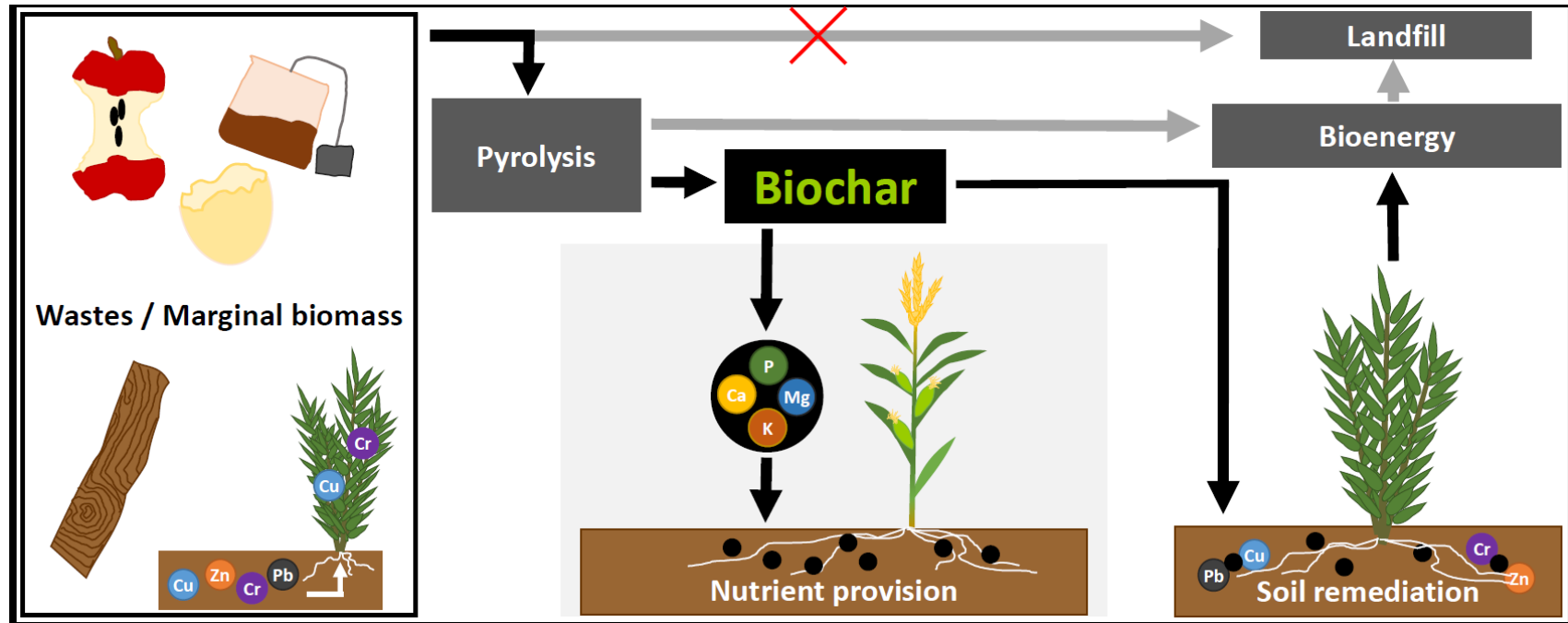
The term “marginal biomass” is used here to describe materials of little or no economic value, e.g. plants grown on contaminated land, food waste or demolition wood. In this study 10 marginal biomass-derived feedstocks were converted into 19 biochars at different highest treatment temperatures (HTT) using a continuous screw-pyrolysis unit. The aim was to investigate suitability of the resulting biochars for land application, judged on the basis of potentially toxic element (PTE) concentration, nutrient content and basic biochar properties (pH, EC, ash, fixed carbon). It was shown that under typical biochar production conditions the percentage content of several PTEs (As, Al, Zn) and nutrients (Ca, Mg) were reduced to some extent, but also that biochar can be contaminated by Cr and Ni during the pyrolysis process due to erosion of stainless steel reactor parts (average +82.8% Cr, +226.0% Ni). This can occur to such an extent that the resulting biochar is rendered unsuitable for soil application (maximum addition +22.5 mg Cr kg⁻¹ biochar and +44.4 mg Ni kg⁻¹ biochar). Biomass grown on land heavily contaminated with PTEs yielded biochars with PTE concentrations above recommended threshold values for soil amendments. Cd and Zn were of particular concern, exceeding the lowest threshold values by 31 fold and 7 fold respectively, despite some losses into the gas phase. However, thermal conversion of plants from less severely contaminated soils, demolition wood and food waste anaerobic digestate (AD) into biochar proved to be promising for land application. In particular, food waste AD biochar contained very high nutrient concentrations, making it interesting for use as fertiliser.

Keywords

Marginal biomass; biochar; potentially toxic element; contaminant; nutrient; pyrolysis

Abbreviations¹

Graphical Abstract



¹ PTE, potentially toxic element; VOC, volatile organic compounds; TGA, thermogravimetric analysis; PAH, polycyclic aromatic hydrocarbons; EC, electric conductivity; AD, anaerobic digestate; IBI, International Biochar Initiative; EBC, European Biochar Certificate

1 Introduction

Produced from biomass in a high-temperature, low-oxygen treatment process, biochar is used in soil for its positive properties for increasing fertility and soil remediation (Lehmann and Joseph, 2009; Sohi et al., 2010). To achieve economically viable biochar production in a sustainable context, the use of waste feedstocks is essential. While crop residues fit into this category, they are not considered to be an ideal feedstock (Shackley et al., 2011). On the other hand, plant material from contaminated sites/phytoremediation as well as non-virgin feedstocks (chemically/biologically transformed, amended or treated material (Shackley et al., 2011)) are resources that need additional treatment before re-use, and so these may be more suited to biochar production.

Large areas of land world-wide have been contaminated by inorganic contaminants, whilst the actual size of the area depends on definition. The scale of the problem is still increasing, so the use of plants from this under-utilised land for conversion into biochar could be a valuable treatment option (Evangelou et al., 2012). Non-virgin feedstocks, such as food waste (anaerobic digestate (AD)), sewage sludge (AD) or demolition wood are also readily-available materials; in the UK alone, around 200 million tonnes of anthropogenic waste is produced annually (DEFRA, 2015). If such wastes could be converted into a valuable resource through pyrolysis, a wide variety of feedstocks would be accessible in large quantities for biochar production. To describe biomass of little economic value the term “marginal biomass” is introduced in this study, taken from the established term “marginal land” for land which, for various reasons, has little agricultural importance (e.g. poor soil quality, pollution) (Peterson and Galbraith, 1932). These marginal biomass-derived feedstocks can be untreated virgin materials such as contaminated plant biomass, or non-virgin feedstocks from chemically/biologically transformed materials.

For biochar application to soil to be acceptable, adverse ecosystem effects need to be avoided and contaminant levels kept to a minimum. The contaminants of concern in biochar are organic compounds that are formed during production and can attach loosely or tightly to the biochar framework (PAHs, VOCs, dioxins) (Buss and Mašek, 2014; Buss et al., 2015; Hale et al., 2012) as well as potentially toxic elements (PTEs) originating from the feedstock (Evangelou et al., 2014; Méndez et al., 2012; Van Wesenbeeck et al., 2014). Total PTE concentrations have been analysed in biochars from virgin biomass sources (materials which have not been chemically/biologically transformed, amended or treated) and the results have not indicated any reasons for concern for soils and plants so far (Freddo et al., 2012; Lucchini et al., 2014a). However, the use of the term “marginal biomass” here describes materials that have a high probability of being somewhat contaminated and predominantly contain elevated levels of PTEs. Thus, the resulting biochars could exceed legislation values applied to soil amendments. This makes it essential to investigate separately the levels of PTEs in each biochar produced from a new,

marginal biomass for compliance with existing regulations. According to the International Biochar Initiative (IBI) (International Biochar Initiative, 2013), arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel and zinc are the PTEs of concern in biochar which, with the exception of cobalt and molybdenum, are also part of the priority pollutant list of the US EPA (Environmental Protection Agency, 1982).

Sewage sludge is a marginal feedstock that could be used for biochar production but often contains elevated levels of PTEs. It is available in large quantities and will be so into the future. For example, in 2008 1.6 million t of sewage sludge was produced in the UK (DEFRA, 2011), which could make commercial biochar production viable. Sewage sludge biochar has already been investigated intensively regarding risks and benefits with variable results, mostly related to its heterogeneity and varying composition (Liu et al., 2014; Luo et al., 2014; Méndez et al., 2012; Van Wesenbeeck et al., 2014; Zielińska and Oleszczuk, 2015). In several recent studies single feedstocks from contaminated biomass were investigated regarding their usefulness for conversion into biochar (Evangelou et al., 2014; Jones and Quilliam, 2014; Lucchini et al., 2014b). However, to our best knowledge, no studies to date have carried out systematic and extensive assessment of PTE in biochars from a range of marginal biomass under different pyrolysis conditions.

Besides PTEs, elements with positive effects on plant growth are present in the ash of feedstocks. The PTEs Cu, Zn, Ni and Mo are phytotoxic in elevated concentrations in soil, in contrast however, low concentrations are needed by plants as micronutrients (Broadley et al., 2011). N, P and K are the major elements in fertilisers and are macronutrients by definition, which means they are the elements needed by plants in high quantities (Hawkesford et al., 2011). All of these nutrients can be found in biochar (Enders and Lehmann, 2012; Mukome et al., 2013). Thus, use of nutrient-rich marginal feedstocks for biochar production could be an alternative way of supplying nutrients to plants through application of the resulting biochar to soil.

During pyrolysis P and K mostly remain in the solid fraction and are therefore applied with the biochar to soil. However, N in the feedstock is mostly evaporated, together with most of the organic material, and this results in a N-poor material (Antal and Grønli, 2003; Liu et al., 2014). During the high temperature treatment of biomass, part of the mineral matrix evaporates as well (Kistler et al., 1987). The “loss” of elements from the solid char material can be beneficial when PTEs are concerned, but are a drawback when nutrients are vaporised (Kistler et al., 1987; Nzihou and Stanmore, 2013). Investigation of volatilisation of elements from pyrolysis solids is essential to select the best suitable production conditions of biochar from mineral-rich feedstocks.

The aim of this research was to investigate whether feedstocks contaminated with PTEs through various routes: (i) plant uptake through soil; (ii) plant uptake through water, and (iii) direct anthropogenic contamination, are suitable for biochar use in soil

in relation to their PTEs compositions. Furthermore, the main objective was to identify the best marginal biomass feedstock for conversion into biochar and the most suitable highest treatment temperature (HTT) judged on the basis of PTE concentrations, nutrient concentrations and basic biochar characteristics (pH, EC, ash, fixed carbon). For this purpose 19 biochars were produced from 10 different materials: feedstocks included various plant species that were grown in PTE contaminated soils, a plant grown in contaminated water and two non-virgin feedstocks.

2 Materials and Methods

2.1 Feedstocks

Ten marginal biomass-derived feedstocks were sourced from five different countries to provide a variety of materials and plant species for biochar production. The feedstocks used were as follows:

Seven biomass samples grown on contaminated land: 1) Wheat straw (*Triticum aestivum*), “WSI” from the village Madlauda (Panipat, Haryana, India) in the vicinity of Panipat thermal power station (coal fired plant; village Assan, Jind road, Panipat, India) and 2) sugarcane bagasse (*Saccharum* spp., species unknown), “SBI” from the vicinity of the river Yamuna close to the village Sarurpur (Uttar Pradesh, India) were sourced from India. Both locations have problems with PTE (and organic) pollution: Panipat thermal power station (Hajarnavis, 2000) and river Yamuna (Mehra et al., 2000). 3) Winter rye straw (*Secale cereal*) (WRB) and 4) willow logs with bark (*salix* spp., species unknown), “WLB” originated from the Campine region in Belgium from heavy metal (Cd, Zn, Pb) contaminated soil (Van Slycken et al., 2013). 5) Whole plant without roots of *Salix purpurea* “SLP”, 6) *Paulonia tomentosa*, “PAT” and 7) *Arundo donax*, “ADX” were sourced from Italian industrial waste sites. *Salix* and *Paulonia* were grown on a site of an old Zn smelter that covers approximately 50 ha near the city of Crotone, Italy (Marchiol et al., 2013). *Arundo donax* was harvested from an industrial area located in Torviscosa from soil contaminated by various metals (Fellet et al., 2007). PTE levels of the various contaminated sites the biomass were sourced from are shown in Table 1 and feedstocks are also listed in Table 2.

One feedstock grew in contaminated waters: 8) Water hyacinth (whole plant) (*Eichhornia crassipes*), “WHI” originated from a municipal waste water drain (Rajiv Nagar, Bhalswa, New Delhi, India) flowing close to Bhalswa Landfill Site, New Delhi which is known for its high levels of contamination (Jhamnani and Singh, 2009; Talyan et al., 2008)

Two non-virgin feedstocks were used: 9) Solid residues from anaerobic digestion of food waste, sourced from the UK, denoted FWD, and containing a high amount of plastics; and 10) heterogeneous, glued, laminated, painted, coated, or otherwise treated demolition wood (without halogenated compounds), sourced from Germany and denoted DW, which included pieces of metal, glass and plastics. The FWD was

autoclaved and dried for several days at 80°C while the DW was shredded to <5 mm particle size prior to pyrolysis.

If not stated otherwise above, feedstocks were dried and shredded with a Bosch AXT Rapid 2200 shredder prior to pyrolysis to give a particle size of around < 30 mm. When very fine and dusty particles were created during the processing the fraction < 2 mm was sieved out and excluded from pyrolysis as the feed and furnace screws were not able to pick up these very fine particles. A sub-sample of the feedstock was dried in an oven at 105°C for 24 h and the moisture content was determined for every run.

2.2 Biochar production

A continuous flow, slow pyrolysis unit was used for biochar production, using an electrically heated split-tube furnace. The feedstock was transported by a screw through the furnace. Figure 1 shows a schematic of the pyrolysis unit. The residence time used corresponds to around 21.5 min in the heated zone for all biochars. Details on the pyrolysis process can be found in SI.

Two feedstocks were pyrolysed at 5 temperatures (350, 450, 550, 650 and 750°C), one at two temperatures (550 and 700°C) and the remaining 7 feedstocks were pyrolysed at 550°C, the typical HTT for biochar production. The biochar yield of SBI 550 could not be determined because the furnace screw did not pick up the straw properly and the exact amount of biomass used could not be measured.

Consequently, the char yield is not reported and mass balances of elements could not be determined. Ten “UKBRC standard biochars” produced with a rotary kiln (described in Buss and Mašek, (2014)) using softwood pellets (SWP), rice husk (RH), oilseed rape pellets (OSR), miscanthus straw pellets (MSP) and wheat straw pellets (WSP) at 550°C and 700°C were used as a reference for comparison of nutrient concentrations.

2.3 TGA, pH and EC

Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo TGA/DSC1 instrument to analyse ash content, fixed carbon and volatile matter according to the method described in Buss and Mašek (2014). Electrical conductivity (EC) and pH were measured according to Rajkovich et al. (2012) using 1 g of crushed biochar (using mortar and pestle) in 20 mL of DI water, which was shaken at 150 rpm for 1.5 h on a bench-top shaker (EC: Hach HQ40d portable meter, conductivity probe meter CDC 401; pH Mettler Toledo FE 30). These analyses were performed in duplicates.

2.4 Elemental analysis of biochar

The biochars were digested according to the modified dry ashing method described as the best total elemental analysis method for biochar by Enders and Lehmann (2012). The method was adjusted in two parameters (more biochar digested, less DI water added in final step) to yield a higher elemental concentration in order to improve the final ICP-OES analysis. Briefly: 0.5 g of each biochar was weighted into

crucibles, heated to 500°C and held for 8 h. After cooling the samples were placed in a steam bath and 5 mL of concentrated HNO₃ was added and evaporated to dryness. After cooling 1 mL HNO₃ and 4 mL H₂O₂ were added and again evaporated to dryness. After cooling, 2 mL HNO₃ was added to dissolve the solids. The resulting solution was filtered through Whatman No. 41 filter paper and the volume increased to 50 mL with deionised water. To ensure accurate comparison, all biochars and the feedstocks were digested using the same method prior to elemental analysis.

The solutions were analysed with an ICP-OES (Perkin Elmer Optima 5300DV) for 20 elements. Most elements were analysed in the axial mode of the instrument, but elements expected to be present in high concentrations (Na, Ca, K, Al, Mg, Fe) were analysed in the radial mode. The ICP multi-element standard solution IV (Certipur®, Merck) (standard 1) covered most of the elements analysed, remaining elements (As, Hg, Mo, P, Se) were combined from single ICP standards to form standard 2. Depending on the range in which the element concentrations fell, calibration curves of three standards (calibration blank, 0.01, 0.1 and 1 ppm), 4 standards (including 10 ppm) or 5 standards (including 100 ppm) were used. The standards 1 and 2 as well as the ICP multi-element standard solution VI (Certipur®, Merck) were used as internal quality control standards for every batch analysed. Reagent blanks were analysed with each batch of extracted biochars.

The detection limits for the various elements are stated in SI Table 1 and were established by running 10 DI water blanks with the respective method (see SI). The digestions and analyses were performed in triplicates (elements As, B, Hg, K, Mo, Na, Se for feedstocks and biochars of DW, FWD, SBI, WHI and WSI, however, are only available in duplicates). Further information, detailed processing of the ICP raw data, calculation of the limit of detection and mass balances can be found in the SI.

2.5 Data analysis

Details on data processing can be found in SI, including statistical tests used.

3 Results and discussion

Ten marginal biomass samples that either grew on/in PTE contaminated land/waters (Table 1) or were biologically/chemically treated feedstocks sourced from 5 different countries were converted into biochar using the same pyrolysis unit (Figure 1) and very similar process conditions. Details on yields and production conditions of all biochars are depicted in Table 2.

3.1 Yields, pH, EC and proximate analysis of biochars

As expected and reported in other studies, the char yield consistently decreased with pyrolysis temperature (Table 2) due to increased loss of volatiles (Antal and Grønli, 2003). Proximate analyses showed a decrease of the volatile matter content with temperature and consequently an increase in fixed carbon content (dry ash-free basis) which is again consistent with general observations in other studies (Crombie et al., 2013; Enders et al., 2012; Jindo et al., 2014; Ronsse et al., 2013; Xie et al., 2015).

The pH values of the biochars strongly increased with pyrolysis temperature and were all in the range of 9 - 10.5, apart from the lower temperature biochars made from demolition wood which had a lower pH (Table 2). In a meta-analysis of biochar studies, biochar has shown to increase the soil pH on average (Biederman and Harpole, 2013). Thus, the biochars with a high pH investigated here can be useful for soil pH elevation and the associated benefits of PTE mobility reduction and improvement of P availability (Biederman and Harpole, 2013). The demolition wood biochars had the lowest ash content and pH values; this relationship of low ash content with pH has already been described in Enders et al. (2012). The electrical conductivity (EC) of the biochars (used for approximation of the salinity) increased with pyrolysis temperature and was well correlated with ash content ($R^2 = 0.7538$; data not shown). WHI 550 had an ash content of over 40% and the highest EC ($8115 \mu\text{S cm}^{-1}$) which originated from the uptake of minerals from a waste water drain by the feedstock, water hyacinth. This biochar and some of the others (e.g. WSI 550, WRB 550, FWD 550) could potentially cause negative effects on plants and soil organisms due to their high salinity if applied in high concentrations.

3.2 Nutrients in biochar

In Table 3 elements are depicted for which statistically significant changes in mass balance from feedstock to biochar were detected. On average around 15% and 10% of the macronutrients Ca and Mg were lost during pyrolysis in all biochars (Mg $p < 0.001$, Ca $p = 0.009$) and for the biochars produced $\geq 700^\circ\text{C}$ around 22.5% of Ca ($p = 0.042$) and 15.4% of Mg (non-significant) was lost, respectively. The loss of macronutrients at typical pyrolysis HTTs indicates that lower temperatures are advisable if greater nutrient retention is desired. However, most importantly, P and K were not lost despite previous reports of K being volatilised during pyrolysis to a higher extent than Ca and Mg (Okuno et al., 2005). In this data set K even increased significantly ($p = 0.041$), however, by 14.1% only (biochars from 8 feedstocks gave

mass balances between +20% and -20% (SI Table 1), only the 2 feedstocks pyrolysed at 5 temperatures had consistently positive mass balances).

The total concentrations of the 4 macronutrients P, K, Mg and Ca are plotted in Figure 2 (micronutrient concentrations can be found in SI Table 2). To provide baseline values, besides the biochars from marginal biomass feedstocks investigated in this study, 10 UKBRC “standard biochars” from 5 conventional, uncontaminated feedstocks pyrolysed at 550°C and 700°C were included. The wood biochars (SWP and DW), as expected, had the lowest concentrations of the 4 reported macronutrients. The elemental content increased with pyrolysis temperature as proportionally more organic material volatilised, while most of the minerals remained in the char. WHI 550 contained a very high concentration of Mg, and while the concentration of Ca was in the same range as for most of the other biochars, P and K concentrations were also elevated. WRB 550 showed comparably high concentrations of P and K but the concentrations of Ca and Mg were in a similar range to most of the other biochars. PAT 550, FWD 550, SLP 550 and WHI 550 all contained levels of macronutrients higher than most of the other biochar samples. In particular, FWD 550 had highly elevated concentrations of P and Ca compared to the other biochars. The total levels of macronutrients in this char were: P 2.0% (w/w), K 2.3%, Ca 9.2% and Mg 0.4%. It has already been shown in early biochar studies that biochar can directly provide nutrients to plants, which can lead to crop yield increases (Lehmann et al., 2003). The key, however, is nutrient availability, and total concentration can only give an indication of this, if at all. Studies showed that biochar has the potential for supplying high amounts of available K to plants, as well as Ca, Mg and micronutrients (Lehmann et al., 2003; Major et al., 2010; Xu et al., 2013). Phosphorus, on the other hand, is reported to be present in available form in slaughterhouse waste, cattle manure and AD sewage sludge biochars and it has been proposed that there is potential for P-rich biochars to act as slow-release fertilisers (Wang et al., 2014; Zwetsloot et al., 2014). These findings suggests that nutrients-rich biochars like FWD 550 can be used as fertilisers on arable soils, as long as PTE levels are not of concern.

3.3 PTEs in biochar

For comparison of PTE levels in biochar, legislation and guideline values were used. Here the values reported are from the “German Biowaste Ordinance” (German Biowaste Ordinance, 1998), the “Swiss Chemical Risk Reduction Act” (Swiss Chemical Risk Reduction Ordinance, 2005) adapted as the EPCC basic and the EPCC premium grade biochar limits (Schmidt et al., 2012), respectively, the European compost and sewage sludge legislation (EU Council Regulation (EEC) No 2092/91, 1991) and the International Biochar Initiative guidelines (originated from legislation from Australia, Canada, EU, UK and the USA) (summarized in SI Table 3).

Arsenic and Hg concentrations in feedstocks and biochars were mostly below detection limits and did not exceed any of the thresholds (Table 4). Only in WHI and

PAT feedstocks and biochar from PAT could As be detected at all (1.63 mg kg^{-1} , 1.22 mg kg^{-1} and 1.96 mg kg^{-1} , respectively). In both biochars the As concentration was lower than theoretically expected, since enrichment through vaporisation of organic matter should result in higher concentrations of minerals than in the feedstock (WHI biochar below detection limit). This finding shows that As was lost during pyrolysis which can be attributed to its low boiling point of 613°C , and has been observed in other studies (Bridle et al., 1990; Helsen et al., 1997; Kim et al., 2012).

Although Al is not mentioned in any of the reported legislation and regulations Al toxicity can be a major problem in acidic soils (Delhaize and Ryan, 1995). In our study, the Al content decreased on average from feedstock to biochar significantly by 35.0% ($p = 0.013$) for all of the biochars investigated in this study (Table 3). A non-significant reduction of 53.2% was observed for the biochars produced at $\geq 700^{\circ}\text{C}$ ($p = 0.077$) (average of only 3 biochars) which is confirmed by findings by Chiang et al. (2014). Although Zn was reduced by 37.5 % ($p = 0.040$) for the 3 biochars produced at $\geq 700^{\circ}\text{C}$ (Table 3) which is similar to findings by Chiang et al. (2014) and Koppolu et al. (2003), Zn threshold values were still exceeded (Table 4, SI Table 3). However, biochars with similar Zn levels from feedstocks also grown on contaminated land have previously shown to result in positive effects on plant shoots, leading the authors to conclude that the increased Zn levels in shoots were beneficial for growth (Evangelou et al., 2014). Besides virgin feedstocks, non-virgin feedstock, e.g. sewage sludge, has been shown to contain Zn contents similar to those in this study (1256 mg kg^{-1}) (Srinivasan et al., 2015). Threshold values for Mo exist only in Canada and the US; none are reported in the various European legislation used for comparison in this study. Still, 5 of the investigated biochars exceeded the reported limit values for Mo (Table 4). Furthermore, several biochars surpass the threshold values for Cd, including the biochars produced from feedstocks from the heavily contaminated sites in Italy and Belgium (Table 4). Overall, no significant change in Cd mass balance was observed on average for all biochars (data not shown), although Cd levels in 4 biochars were reduced by more than 80% compared to the feedstock (SI Table 1). Volatilisation of Cd from pyrolysis solids is frequently reported in literature, specifically at temperatures above 600°C (Chiang et al., 2014; Evangelou et al., 2014; Kistler et al., 1987; Luo et al., 2014). Yet, for example in Liu et al. (2014), Cd remained in the char to the highest extent in comparison with various other PTEs (Cu, Pb, Zn, Cr). In general, volatilisation of elements is not simply a function of temperature but differs according to elemental concentrations in the feedstock and is influenced by interactions with the other inorganic and organic components, which explains the high fluctuations of the same elements in different feedstocks in this study (SI Table 1) (Cuypers and Helsen, 2011; Okuno et al., 2005; Olsson et al., 1997; Van Wesenbeeck et al., 2014).

Ni and Cr have also been reported to vaporise during pyrolysis (Kistler et al., 1987; Koppolu et al., 2003). Interestingly however, for these elements and Fe, even significant increases have been observed (Table 3). Cr increased by 82.8%, Fe by

207.2% and Ni even by 226.0% on average for all biochars, which indicates contamination during pyrolysis. This can be a result of erosion of small amounts of metal from reactor walls by feedstock and biochar in the continuous pyrolysis unit used in this study. We propose that the friction caused by the pressure the moving furnace screw applied onto the material in the furnace eroded small steel particles which contaminated the biochar. As the reactor is made of a high grade stainless steel 253MA (contains 21% chromium and 11% nickel), such a contamination path is probable. It has already been indicated in the EBC quality guidelines that there is potential for this to happen, specifically in new pyrolysis units (Schmidt et al., 2012). All in all, this is an important point to consider as, for example, DW 650 and 750 would not be allowed to be applied on Swiss soils due only to the exceedance of Cr limit values and SBI 550 due only to Ni exceedance (EBC premium grade limit, Table 4).

To further elucidate whether the Ni and Cr exceedances were only attributed to erosion of Ni and Cr from steel in the pyrolysis unit, in contrast to percentage change as above, additional calculations were undertaken. The change in concentration of elements after pyrolysis compared to the expected concentration with the scenario of 100% elemental retention in mg kg^{-1} was calculated (SI Table 1). This was done specifically to investigate how much Ni and Cr in the biochars could be attributed to contamination with these elements during the pyrolysis process. The deviation in concentrations expected (100% elemental retention) to actual concentrations for Ni were up to 45 mg kg^{-1} and up to $16\text{-}22 \text{ mg kg}^{-1}$ for Cr. Considering the legislation / guideline values for Ni of $30\text{-}50 \text{ mg kg}^{-1}$ and for Cr of $80\text{-}100 \text{ mg kg}^{-1}$ (Table 4), this shows Ni and Cr enrichment from steel during pyrolysis can cause exceedance of threshold values. To overcome this, a rotary drum could be used to replace the furnace screw (which puts a lot of pressure on the furnace metal), or the Ni-Cr steel of the screw could be replaced by a different steel. However, these results show that the exceedance of guideline values (e.g. SBI 550) can be avoided by using a different pyrolysis unit and the feedstock itself is not a concern regarding these PTEs.

In the 19 biochars investigated here, the PTEs Zn and Cd in particular cause problems with exceedance of threshold values, The highest Zn and Cd concentrations exceed the lowest guideline values (compost guideline) by 7-fold and 31-fold, respectively (Table 4, SI Table 3). The feedstocks resulting in biochar that caused exceedances here originated from soil that is known for its contamination with these elements. Pb, Cu, As and Hg did not exceed biochar guideline values despite the fact that some of the land the plants were grown exceed soil guideline values (Table 1). A fraction of As, Hg, Zn and Al from feedstocks were lost from pyrolysis solids, which can be beneficial for biochar soil application, yet, it must be ensured that these PTEs are not released into the environment as vapours during pyrolysis. In addition to Zn and Cd, concentrations of Ni and Cr in some biochars exceed legislation values which can be traced back to the biochar production process itself.

3.4 Effect of temperature on concentration of PTEs in biochar

One virgin feedstock, *Arundo donax* (plant biomass from PTE contaminated land), and one non-virgin feedstock, demolition wood, were pyrolysed at 5 temperatures in the range 350-750°C. As discussed in 3.1, increasing pyrolysis temperatures decreased the volatile matter content of the biochars and increased the fixed carbon and ash content (Table 2). Volatile organics vaporised, while most of the ash / PTEs remained. This led to enrichment of PTEs in the biochar and a higher concentration of PTEs compared to the feedstock (Table 4). However, some PTEs partially evaporated at the applied temperatures, reducing their concentration, e.g. Zn for DW and ADX (Table 4). Elements such as Cu did not evaporate and, due to this enrichment, the biochars produced at highest pyrolysis temperatures had the highest Cu concentrations (ADX 650 and 750 not significantly different). Consequently, the effect of temperature on the concentration of PTEs in biochar is not only dependent on the element under investigation but also on the feedstock matrix, which, as discussed in 3.3, affects the evaporation behaviour of the elements. However, the parameter which influences the concentration of PTEs in biochar most is their concentration in the initial material. Thus, appropriate selection of feedstock is the most crucial parameter for production of biochar with low total concentrations of PTEs (Kookana et al., 2011).

3.5 Environmental implications of marginal biomass-derived biochar

3.5.1 Biochars unsuitable for soil application

Although water hyacinth biochar (WHI 550) contained high concentrations of nutrients, it also contained a very high ash content which could lead to salinity-related toxic effects. Despite having lost large amounts of PTEs during pyrolysis (SI Table 1), the concentrations of Cr, Cu, Ni, Pb and Zn greatly exceeded threshold values (Table 4, SI Table 3). It is known that water hyacinth can take up and accumulate large amounts of toxic substances from water, making it interesting for waste water treatment (Mehra et al., 2000), however this is a clear disadvantage for its use in biochar production.

Willow logs, winter rye, *Salix purpurea* and *Paulonia tomentosa* all originated from contaminated sites where soil PTE concentrations exceed legislation values (campine region in Belgium, region of an old Zn smelter in Italy) (Table 1) (EU Council Directive 86/278/EEC, 1986; German Federal Soil Protection Act, 1999). The biochars produced from these feedstocks all exceeded Cd and Zn legislation values and the IBI guideline values for Mo. Again, the ability of willow to accumulate Cd is useful for phytotextraction but here it shows that, when grown on Cd contaminated land, willow is unsuitable to use for biochar production for soil application (Van Slycken et al., 2013).

From this it can be concluded that it is not advisable to use plants grown on soil that already exceeds legislation values or plants from polluted waters for biochar production, although exceedance of biochar threshold values does not always occur. Specifically, the use of plant species capable of accumulating high amounts of PTEs

as feedstock for biochar is problematic. Instead, as described in Evangelou et al. (2012) and Witters et al. (2012), since plants grown on heavily contaminated land are not competing with crops for human consumption they have high potential to be used for sustainable energy production.

3.5.2 Biochars with little concern for application

The biochars from wheat straw (WSI) grown at a site close to a thermal power plant (India), and sugarcane bagasse (SBI) that grew close to the highly polluted river of Yamuna (India) in PTE contaminated soil (Table 1) comply with regulations and have mostly moderate levels of nutrients along with medium to high pHs. The biochars from the woody materials, demolition wood and *Arundo donax*, showed rather low concentrations of macronutrients and no relevant exceedances of threshold values, despite *Arundo donax* having grown on a metal contaminated site that is close to PTE threshold values for soil (Table 1).

Overall, as also concluded in Nzihou and Stanmore (2013) for combustion ash from similar materials, biochars from feedstocks grown on less heavily contaminated land and demolition wood biochars seem safe to apply on soil. Therefore the high temperature biochars from these feedstocks can be suitable for increasing soil pH when applied in high doses (Biederman and Harpole, 2013), for immobilising metals (Uchimiya et al., 2010), and for carbon sequestration due to their recalcitrance indicated by their high fixed carbon contents (which can be used as a proxy for carbon stability) (Crombie et al., 2013). Consequently, these biochars could be used for remediation of contaminated land (e.g. the land the feedstocks were sourced from) by immobilising PTEs, improving soil properties and subsequently increasing plant yields (Buss et al., 2012).

3.5.3 Biochar with high potential for soil application

Anaerobically digested food waste biochar (FWD 550) not only complied with EBC guideline values for heavy metal content, it also showed high concentrations of all the 4 macronutrients measured. This is a significant finding as around 16 million tonnes of food waste are produced every year in the UK alone (DEFRA, 2011). However, it is important to keep in mind that the composition of food waste can differ widely. Nevertheless, this makes food waste (AD) a very suitable marginal feedstock that is available in large quantities for the production of biochar and subsequent application on soil, as long as the nutrients in the biochar are plant available, something that should be tested in future work.

4 Conclusions

In this study 10 marginal biomass-derived feedstocks from either contaminated land/waters or non-virgin biomass were investigated for their suitability for biochar production. First, it was shown that at typical pyrolysis temperatures some PTEs (e.g. As, Al, Zn) and nutrients partially evaporated from the mineral-rich materials. Using higher pyrolysis temperatures was found to be unsuitable as the macronutrients Mg and Ca were increasingly lost. In addition, feedstocks grown on industrial waste sites and in heavily PTE contaminated water bodies were found to be unsuitable for biochar production due to exceedance of PTE threshold values. Biochars produced from biomass grown in less contaminated soils and two biologically/chemically converted materials did comply with regulations and appear to be safe to apply to soils. Finally, food waste AD was found to be the best marginal feedstock for biochar production due to very high concentrations of plant macronutrients, making the resulting biochar a promising potential organic fertiliser. Our results showed that the long-standing assumption that contamination issues in biochar were either attributed to organic compounds formed during pyrolysis or inorganic PTEs originating in the feedstock is not always valid. We have shown that another source of contaminants can be present, namely contamination by Ni and Cr from high grade steel used in some high-temperature reactors. This finding has important consequences for the design and operation of industrial biochar production units.

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Table 1: PTE concentrations of soils in the area the biomass used for biochar production grew. No data for the region of wheat straw (India) was available; water hyacinth (India) was grown in a waste water drain.

plant	location	reference		As	Cd	Cu	Hg	Ni	Pb	Zn
		lower soil limit EU #	mg kg ⁻¹		1.00	50		30	30	150
		soils limit Germany *	mg kg ⁻¹	200			5			
sugarcane	Sarurpur, India	Mehra et al., 2000	mg kg ⁻¹		0.46	18		13	16	47
willow, winter rye	campine region, Belgium	van Slycken et al., 2013	mg kg ⁻¹		6.50					377
<i>Salix purpurea</i> , <i>Paulonia tomentosa</i>	Crotone, Italy	Marchiol et al., 2013	mg kg ⁻¹	242	498	1535	32		5802	44048
<i>Arundo donax</i>	Torviscosa, Italy	Fellet et al., 2007	mg kg ⁻¹	20	0.83	73			22	97

EU Council Directive 86/278/EEC 1986, ANNEX 1 A, on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture

* German Federal Soil Protection Act 1999, Annex 2, 2.2, Guidance values for contaminant transfer soil-crop on agricultural fields in regards to plant quality

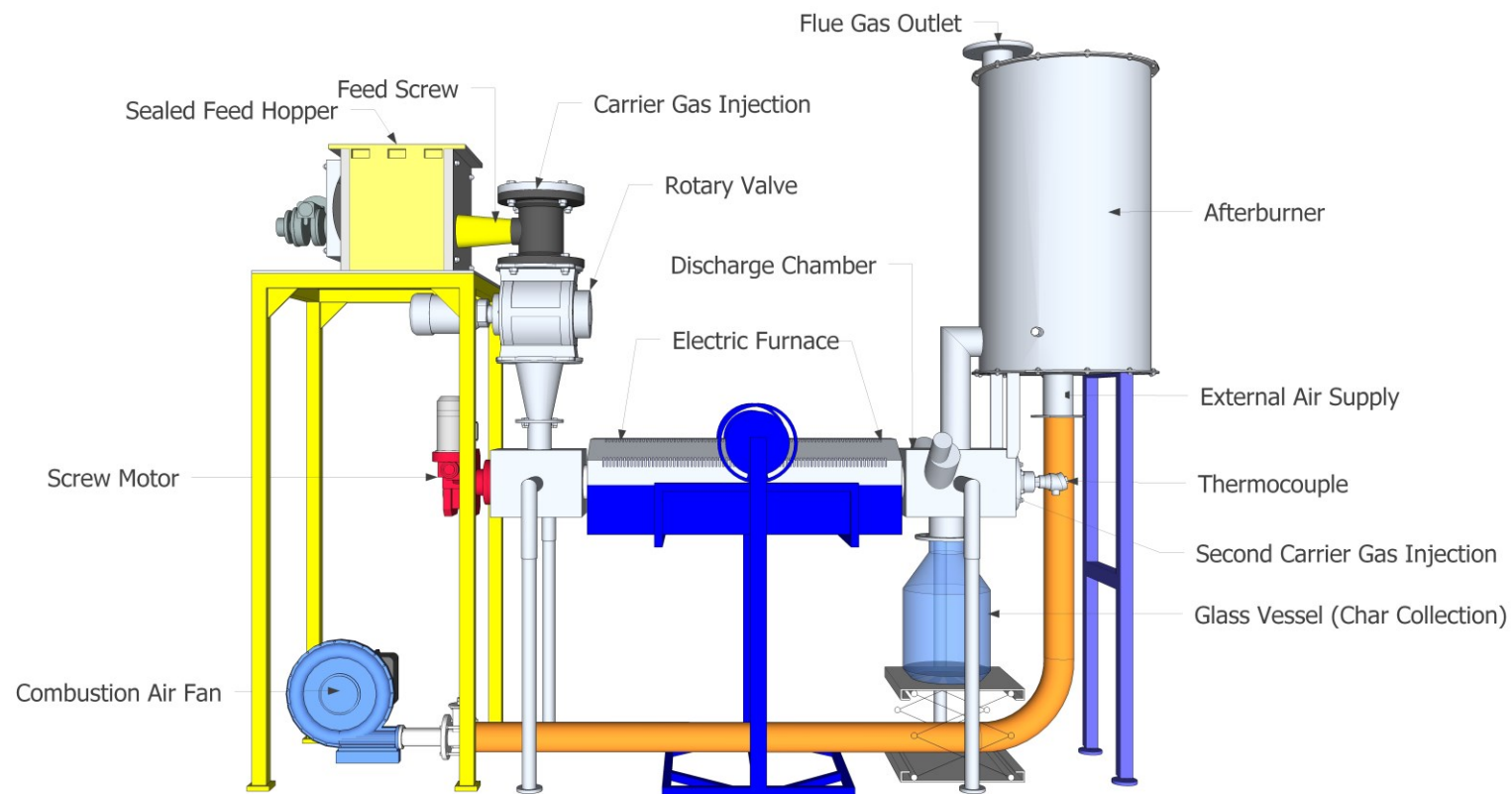


Figure 1: Continuous screw-pyrolysis unit (UKBRC stage II unit).

Table 2: Selected production conditions and biochar properties of 19 biochars investigated in this study. Proximate analysis (volatile matter, fixed carbon, ash), pH and electric conductivity (EC) were performed in duplicates and averages \pm standard deviations are shown.

biochar	feedstock	HTT °C	FR g h ⁻¹	yield % db	volatile matter % daf	fixed carbon % daf	ash % db	pH	EC $\mu\text{S cm}^{-1}$
DW									
DW 350	Demolition wood, Germany	350	500	31.60	28.90 \pm 1.63	71.10 \pm 1.63	5.35 \pm 0.78	7.56 \pm 0.39	175 \pm 18
DW 450	Demolition wood, Germany	450	500	28.61	23.44 \pm 0.91	76.56 \pm 0.91	3.51 \pm 0.92	7.78 \pm 0.30	212 \pm 25
DW 550	Demolition wood, Germany	550	500	25.51	14.72 \pm 0.26	85.28 \pm 0.26	5.32 \pm 0.01	7.65 \pm 0.08	189 \pm 29
DW 650	Demolition wood, Germany	650	500	22.16	10.17 \pm 0.52	89.83 \pm 0.52	4.97 \pm 0.49	8.48 \pm 0.11	206 \pm 17
DW 750	Demolition wood, Germany	750	500	19.95	8.25 \pm 1.78	91.75 \pm 1.78	5.70 \pm 2.48	9.85 \pm 0.27	408 \pm 37
ADX									
ADX 350	<i>Arundo donax</i> , Italy	350	500	38.69	33.72 \pm 0.79	66.28 \pm 0.79	12.38 \pm 0.90	8.79 \pm 0.44	1095 \pm 306
ADX 450	<i>Arundo donax</i> , Italy	450	500	30.13	21.83 \pm 0.55	78.17 \pm 0.55	12.62 \pm 0.92	9.84 \pm 0.11	2165 \pm 191
ADX 550	<i>Arundo donax</i> , Italy	550	500	26.24	17.13 \pm 0.34	82.87 \pm 0.34	14.75 \pm 0.43	9.68 \pm 0.21	2580 \pm 85
ADX 650	<i>Arundo donax</i> , Italy	650	500	25.49	14.10 \pm 1.10	85.90 \pm 1.10	16.01 \pm 2.47	10.13 \pm 0.41	2915 \pm 78
ADX 750	<i>Arundo donax</i> , Italy	750	500	22.95	10.84 \pm 0.22	89.16 \pm 0.22	15.51 \pm 0.84	10.61 \pm 0.64	3430 \pm 269
SBI 550	Sugarcane bagasse, India	550	250	*	16.84 \pm 0.43	83.16 \pm 0.43	12.91 \pm 0.48	9.34 \pm 0.03	954 \pm 153
WHI 550	Water hyacinth, India	550	400	45.20	43.39 \pm 3.75	56.61 \pm 3.75	42.92 \pm 4.16	9.85 \pm 0.11	8115 \pm 389
WSI 550	Wheat straw, India	550	250	30.74	21.87 \pm 1.68	78.13 \pm 1.68	24.55 \pm 1.10	10.12 \pm 0.01	6385 \pm 431
WLB									
WLB 550	Willow logs, Belgium	550	500	26.68	16.38 \pm 0.14	83.62 \pm 0.14	7.22 \pm 0.89	9.52 \pm 0.16	192 \pm 23
WLB 700	Willow logs, Belgium	700	500	23.78	10.85 \pm 0.27	89.15 \pm 0.27	8.37 \pm 1.78	9.52 \pm 0.11	620 \pm 49
WRB 550	Winter rye straw, Belgium	550	225	20.76	21.93 \pm 1.04	78.07 \pm 1.04	15.92 \pm 1.28	10.10 \pm 0.62	6330 \pm 42
SLP 550	<i>Salix purpurea</i> , Italy	550	350	35.79	27.25 \pm 0.39	72.75 \pm 0.39	22.21 \pm 0.62	10.15 \pm 0.49	1678 \pm 177
PAT 550	<i>Paulonia tomentosa</i> , Italy	550	350	34.40	29.98 \pm 2.99	70.02 \pm 2.99	21.12 \pm 0.21	10.55 \pm 1.09	3150 \pm 170
FWD 550	Food waste digestate, UK	550	150	28.79	30.07 \pm 0.99	69.93 \pm 0.99	26.85 \pm 0.58	8.88 \pm 0.24	5580 \pm 438

*not available, see materials and methods

HTT, highest treatment temperature

FR, feeding rate during pyrolysis

yield, char yield during pyrolysis

db, dry basis; daf, dry ash free basis

AV, average; SD, standard deviation

Table 3: Relative changes of elemental content from feedstock to biochar after pyrolysis (%). Geometric means and geometric standard deviations (SD) were calculated for biochars produced at all temperatures and only the ones produced $\geq 700^{\circ}\text{C}$. One sample, two tailed t-tests were performed to identify significant changes of the ln transformed data ($p < 0.05$) (Details in SI). Only the elements that showed significant changes are depicted here.

			Al	Ca	Cr	Fe	K	Mg	Ni	Zn
all biochars	geometric mean	%	-35.0	-14.1	82.8	207.2	14.1	-9.7	226.0	-13.7
	- geometric SD	%	32.3	16.1	108.5	197.0	23.8	12.5	227.7	21.3
	+ geometric SD	%	64.2	19.9	266.9	549.4	30.0	14.5	754.9	28.4
	n		17	17	17	17	17	17	17	17
	p - value		0.013*	0.009*	0.012*	0.000*	0.041*	0.000*	0.001*	0.056
biochars produced $\geq 700^{\circ}\text{C}$	geometric mean	%	-53.2	-22.5	82.634	160.97	19.515	-15.4	397.54	-37.5
	- geometric SD	%	15.0	6.9	98.87	110.64	35.87	7.6	393.00	9.7
	+ geometric SD	%	22.1	7.5	215.57	192.08	51.25	8.3	1870.33	11.4
	n		3	3	3	3	3	3	3	3
	p - value		0.077	0.042*	0.313	0.095	0.478	0.091	nt	0.040*

* significantly different ($p < 0.05$)

' exponentially back-transformed before statistically analysed

nt, not tested

n, number of biochars

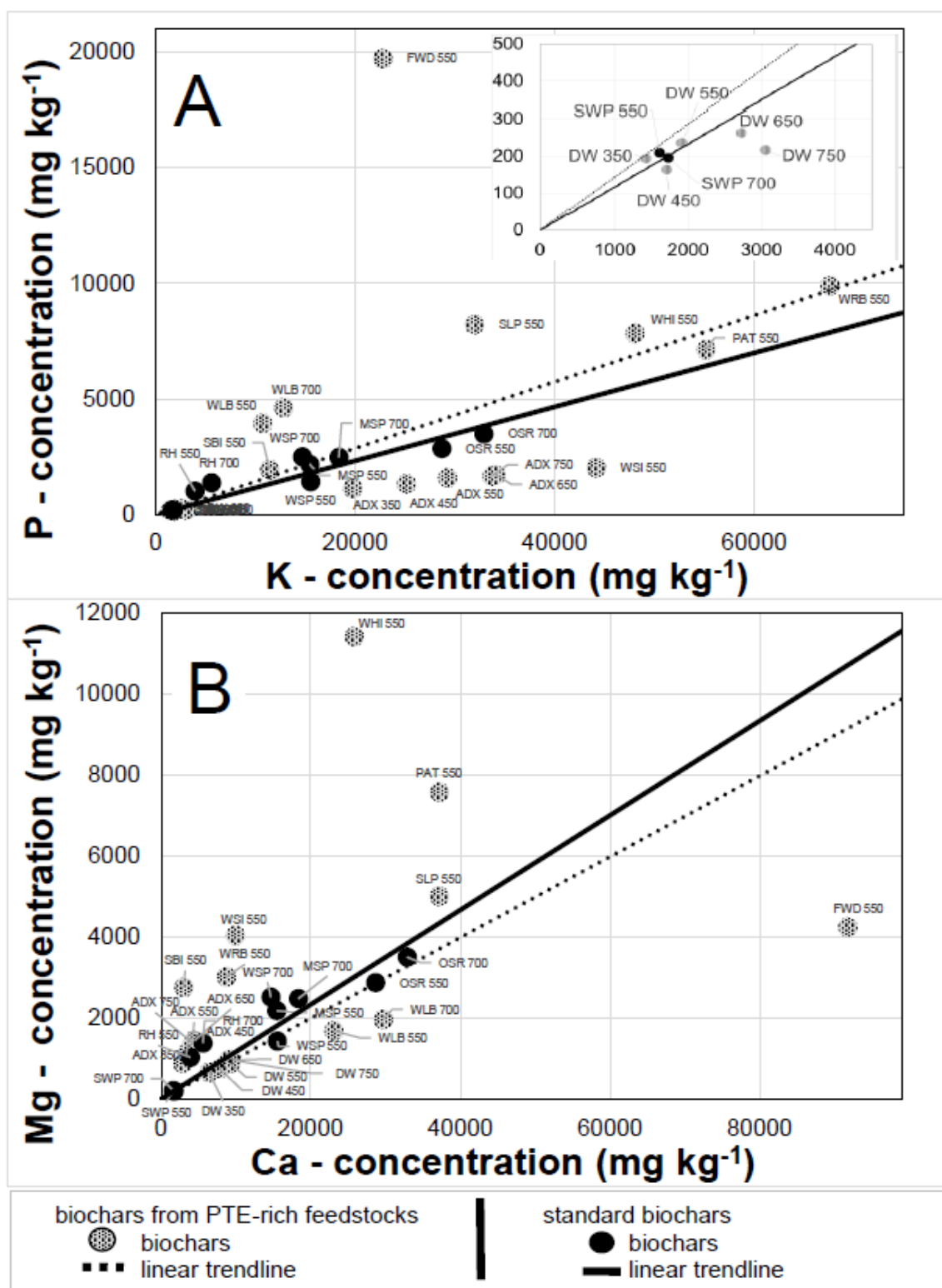


Figure 2: Total concentrations (mg kg^{-1}) of macronutrients P and K (upper figure, A) and Mg and Ca (lower figure, B) in 19 biochars. In addition, 10 UKBRC standard biochars are plotted for comparison.

Table 4: Potentially toxic element (PTE) concentrations (mg kg⁻¹) of 19 biochars and their 10 feedstocks with averages and standard deviations.

		As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn
DW	mg kg ⁻¹	< 0.72	< 0.04	0.27 ± 0.18	15.96 ± 8.33	10.36 ± 6.49	< 0.23	< 0.21	1.69 ± 0.94	35.25 ± 29.30	40.29 ± 3.96
DW 350	mg kg ⁻¹	< 0.72	0.50 ± 0.46	0.51 ± 0.11	35.86 ± 5.12	34.70 ± 19.62	< 0.23	0.28 ± 0.31	10.18 ± 1.03	48.63 ± 20.46	117.69 ± 15.78
DW 450	mg kg ⁻¹	< 0.72	0.22 ± 0.19	1.19 ± 0.97	47.44 ± 8.90	34.71 ± 4.57	< 0.23	< 0.21	8.01 ± 0.48	62.15 ± 12.37	150.15 ± 14.89
DW 550	mg kg ⁻¹	< 0.72	0.19 ± 0.18	0.78 ± 0.13	55.92 ± 9.18	35.68 ± 4.18	< 0.23	< 0.21	12.62 ± 3.92	66.50 ± 9.80	167.30 ± 20.34
DW 650	mg kg ⁻¹	< 0.72	0.33 ± 0.36	1.02 ± 0.12	94.54 ± 4.99	46.38 ± 2.65	< 0.23	< 0.21	38.48 ± 7.92	149.56 ± 123.82	236.84 ± 136.75
DW 750	mg kg ⁻¹	< 0.72	0.12 ± 0.11	2.08 ± 2.18	82.16 ± 15.61	53.16 ± 10.35	< 0.23	< 0.21	16.62 ± 1.30	35.71 ± 8.15	105.91 ± 9.63
ADX	mg kg ⁻¹	< 0.72	0.05 ± 0.05	< 0.08	< 0.49	1.58 ± 0.70	< 0.23	< 0.21	0.47 ± 0.25	< 0.74	11.87 ± 3.97
ADX 350	mg kg ⁻¹	< 0.72	0.92 ± 0.24	0.25 ± 0.04	6.08 ± 3.91	6.72 ± 0.95	< 0.23	0.56 ± 0.61	8.33 ± 2.37	1.43 ± 2.47	42.02 ± 8.11
ADX 450	mg kg ⁻¹	< 0.72	0.11 ± 0.02	0.16 ± 0.04	2.31 ± 2.74	5.89 ± 0.78	< 0.23	0.28 ± 0.49	3.39 ± 0.92	37.70 ± 62.57	38.16 ± 4.36
ADX 550	mg kg ⁻¹	< 0.72	0.98 ± 0.12	0.21 ± 0.04	5.67 ± 2.83	6.54 ± 0.66	< 0.23	0.58 ± 0.84	7.06 ± 1.07	5.30 ± 9.18	40.84 ± 4.40
ADX 650	mg kg ⁻¹	< 0.72	2.70 ± 0.18	0.28 ± 0.06	8.47 ± 2.08	7.73 ± 0.49	< 0.23	1.40 ± 0.79	9.35 ± 0.43	1.73 ± 2.99	48.85 ± 4.34
ADX 750	mg kg ⁻¹	< 0.72	2.64 ± 0.55	0.16 ± 0.05	2.85 ± 2.09	7.46 ± 1.14	< 0.23	0.54 ± 0.47	4.22 ± 0.89	27.22 ± 42.73	37.89 ± 5.64
SBI	mg kg ⁻¹	< 0.72	< 0.04	0.37 ± 0.32	4.28 ± 3.74	2.14 ± 0.34	< 0.23	< 0.21	3.26 ± 0.49	19.37 ± 33.55	8.19 ± 2.45
SBI 550	mg kg ⁻¹	< 0.72	0.47 ± 0.42	0.90 ± 0.28	24.21 ± 7.42	13.98 ± 6.59	< 0.23	0.92 ± 0.13	37.89 ± 13.74	4.73 ± 1.94	39.77 ± 9.21
WHI	mg kg ⁻¹	1.63 ± 0.12	1.24 ± 0.86	9.81 ± 5.15	173.62 ± 29.43	105.57 ± 8.08	< 0.23	6.07 ± 0.37	88.81 ± 1.48	100.86 ± 15.27	262.06 ± 19.83
WHI 550	mg kg ⁻¹	< 0.72	0.45 ± 0.39	7.44 ± 0.30	176.42 ± 18.81	118.85 ± 7.41	< 0.23	7.70 ± 0.44	110.59 ± 4.56	215.10 ± 154.13	392.82 ± 35.25
WSI	mg kg ⁻¹	< 0.72	< 0.04	0.35 ± 0.05	14.35 ± 12.43	2.17 ± 0.17	< 0.23	2.55 ± 0.21	1.41 ± 0.72	< 0.74	2.65 ± 1.25
WSI 550	mg kg ⁻¹	< 0.72	0.05 ± 0.05	1.17 ± 0.20	17.83 ± 13.80	16.55 ± 1.54	< 0.23	8.51 ± 0.35	26.32 ± 1.99	5.98 ± 2.66	62.00 ± 9.03
WLB	mg kg ⁻¹	< 0.72	11.46 ± 0.07	0.09 ± 0.02	< 0.49	6.91 ± 0.33	< 0.23	< 0.21	0.36 ± 0.22	16.27 ± 2.15	513.64 ± 64.20
WLB 550	mg kg ⁻¹	< 0.72	8.29 ± 0.50	0.29 ± 0.11	3.98 ± 3.56	16.46 ± 0.54	< 0.23	1.65 ± 2.64	16.73 ± 4.42	42.57 ± 7.65	1230.45 ± 98.92
WLB 700	mg kg ⁻¹	< 0.72	7.32 ± 0.72	0.48 ± 0.01	9.13 ± 2.25	19.95 ± 0.81	< 0.23	0.31 ± 0.54	45.96 ± 4.52	45.87 ± 17.94	1375.12 ± 30.58
WRB	mg kg ⁻¹	< 0.72	2.70 ± 0.03	0.16 ± 0.02	1.60 ± 2.77	9.07 ± 0.30	< 0.23	1.94 ± 0.22	0.48 ± 0.13	24.99 ± 17.78	295.75 ± 33.90
WRB 550	mg kg ⁻¹	< 0.72	6.82 ± 0.27	0.42 ± 0.02	6.98 ± 2.90	25.72 ± 1.14	< 0.23	9.48 ± 0.81	14.51 ± 2.62	21.95 ± 5.22	810.89 ± 25.73
SLP	mg kg ⁻¹	< 0.72	48.86 ± 3.60	0.57 ± 0.03	0.83 ± 1.44	8.14 ± 0.36	< 0.23	0.52 ± 0.90	0.78 ± 0.10	20.71 ± 27.73	629.87 ± 43.78
SLP 550	mg kg ⁻¹	< 0.72	22.00 ± 0.75	2.19 ± 0.09	13.13 ± 3.60	52.22 ± 1.11	< 0.23	7.85 ± 0.54	18.89 ± 2.28	42.03 ± 5.68	1404.33 ± 33.33
PAT	mg kg ⁻¹	1.22 ± 0.23	6.71 ± 1.21	0.23 ± 0.05	< 0.49	13.39 ± 2.57	< 0.23	< 0.21	1.07 ± 0.08	29.04 ± 32.54	208.63 ± 33.52
PAT 550	mg kg ⁻¹	1.96 ± 0.81	19.13 ± 1.27	1.36 ± 0.08	17.68 ± 3.40	47.71 ± 1.37	< 0.23	5.48 ± 0.23	24.08 ± 3.17	48.06 ± 17.14	544.68 ± 4.39
FWD	mg kg ⁻¹	< 0.72	< 0.04	0.49 ± 0.09	6.34 ± 4.22	14.38 ± 0.98	< 0.23	0.51 ± 0.58	15.49 ± 2.35	35.61 ± 42.09	56.41 ± 2.27
FWD 550	mg kg ⁻¹	< 0.72	< 0.04	2.76 ± 1.54	25.05 ± 6.33	45.71 ± 2.88	< 0.23	1.15 ± 0.01	10.21 ± 0.74	15.12 ± 4.06	218.77 ± 17.63

